Study on the Impact of Biomass Burning on Chemical Composition of Aerosols in the Atmosphere of Agra

A

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Introduction

Air pollution today is a global epidemic and is one of the world's biggest health hazards, contributing to about 7 million premature deaths annually. Most recently it has been estimated that the increase in the number of premature deaths in Indian cities has reached around 1, 00,000 from exposure to air pollution (Vohra et al., 2022). Compounding this staggering health crisis, air pollution is also estimated to cost the global economy upwards of $2.9 trillion per year (3.3% of global GDP) due to fossil fuel emissions alone, while also contributing to a range of severe environmental problems. A critical component of air pollution is atmospheric particulate matter (PM) which includes fine particles with small diameters that remain suspended in air and do not settle. PM is intrinsically linked to adverse human health and environmental impacts, it has been extensively studied for its chemical composition, spatial and temporal variations, sources, climatic effects and health impacts (Sinha et al., 2022; De Oliveria Alves et al., 2014). Recent studies have revealed that the chemical composition and morphology of these particulates is influenced by size, sources, precursors, local and regional meteorology. Hence considerable uncertainties are associated with the quantification of feedback of particulates to both climate system and human health. Hence in order to establish adverse impacts of airborne particulate with high level of certainty and to improvise an effective air quality management plan; it is necessary to identify particulate sources and variations, both in terms of space and time.

As per the recent studies, the analysis of the variation of ozone (O_3), carbon monoxide (CO), sulphur dioxide (SO_2) and chemical composition (ionic constituents, metals and polyaromatic hydrocarbons) of $PM_{2.5}$ and PM_{10} alongwith the meteorological parameters have shown higher concentrations during winter and the haze events associated with lower temperature, low wind speed and high relative humidity (Verma et al., 2017; Sah et al., 2018; Sah et al., 2019a Sah et al., 2019b; Agarwal et., 2020; Kumari et al., 2020; Kumari et al., 2021a; Kumari et al., 2021b; Mangal et al., 2021; Satsangi et al., 2021; Verma et al., 2021). In particular, during the haze events the aerosol composition showed a higher contribution (~84%) of Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ to total soluble ions suggesting secondary aerosol formation during haze events (Kumari et al., 2021). Backward air mass trajectories and potential source contribution function (PSCF) suggested crop residue burning activities and stable synoptic meteorology played a significant role affecting the haze events (Kumari et al., 2021) due to

interactions between anthropogenic emissions and atmospheric processes.

Another aspect of deteriorating air quality is biomass burning (BB). According to numerous studies, biomass burning has always been a significant contributor to depleting air quality and exacerbating health problems. Biomass burning includes wildfires, agricultural fires, prescribed fires, and anthropogenic bioenergy usage (wood burning, heating oil use, and coal-fired power plants for electricity production), and it is primarily composed of carbonaceous aerosol (i.e., organic carbon (OC) and elemental carbon (EC) (Masiol et al., 2017; Squizzato et al., 2018; Lee and Chan, 2015).

Residential biomass burning (BB) as a source of heating or cooking alongwith other anthropogenic biomass burning emissions like industrial emissions, are becoming an increasingly important source of organic aerosols (OA) in urban environments when stricter controls on fossil fuel combustion are implemented (Pandis et al., 2016; Florou et al., 2017; O'Dell et al., 2019). Furthermore, as a result of climate change, the frequency of smoke-impacted days in urban areas is increasing (O'Dell et al., 2019; Ford eta al., 2018).

Biomass burning (BB) in particular emits a wide range of primary organic aerosols (POAs) and gaseous-phase volatile organic compounds (VOCs) which undergo rapid and complex photochemical reactions, resulting in the formation of secondary organic aerosols (SOAs). Some POAs are semi-volatile in nature and evaporate to contribute to gas-phase abundances of labile VOCs during long-range transport and undergo photochemical processing in the atmosphere and also interact with anthropogenic pollutants such as O_3, OH^-, and NO_x to produce SOAs. These VOCs can disperse during downwind transport away from the source under favourable meteorological conditions than POAs. Consequently, the POA fraction dominates the BB-derived organic aerosols within the source emissions and the SOA component increases significantly during transport. Despite numerous efforts in recent years to understand the relative significance of POA versus SOA, knowledge regarding the chemical and physical evolution of biomass burning organic aerosols (BBOA) is still limited. Probing the evolution of BBOAs over continental sites is somewhat complicated by the inadvertent mixing of source emissions and processing effects.

Thus, in order to estimate the impact on air quality and human health, it is necessary to better understand the different sources of air pollutants in the atmosphere. Conventionally, potassium has

been extensively used as an inorganic biomass tracer to apportion BB contributions to ambient PM (Chen et al., 2017). Potassium (K) is a significant constituent of fine particulate matter. There are numerous sources of potassium emissions in the atmosphere, including sea salt, cooking, dust, coal combustion, and waste incineration (Lawson et al., 1979; Andreae, 1983; Watson et al., 2001; Schauer et al., 2002). However, K emitted from soil and dust is mostly insoluble in water, especially when alumina-silicate minerals are present (Andreae, 1983). According to several studies, coal combustion may also emit K and K^+ into the atmosphere (Wang et al., 2009, 2014). K^+ has traditionally been used as a tracer for biomass burning in receptor models (Zhang et al., 2013a, b; Tao et al., 2014). Several studies have also used ratios such as $K^+/PM_{2.5}$, EC/K^+, and K^+/OC to estimate biomass burning's contribution to ambient aerosol (Duan et al., 2004; Li et al., 2007; Park et al., 2013; Zhou et al., 2017). However, these methods were based on the assumption that K (or K^+) was derived solely from biomass burning and that K (or K^+) emission factors were unaffected by other conditions (e.g., fuel types and combustion conditions) (Yan et al., 2017). Although most studies estimated the contribution of biomass burning based on K or K^+, a few studies reported that K was not an ideal tracer for biomass burning and could only be used as an appropriate biomass burning indicator when the majority of K or K^+ was emitted from biomass burning. As a result, there is a need for alternative compounds or elements to estimate the sources of biomass burning.

Diacids in aerosols may be primarily emitted from fossil fuels combustion (Kawamura and Kaplan, 1987; Wang and Kawamura et al., 2006; Ho et al., 2007; van Pinxteren et al., 2014;) and biomass burning (Narukawa et al., 1999) or formed as secondary organic aerosols from atmospheric oxidation of unsaturated fatty acids (Kawamura et al., 1996) and cyclic alkenes (Hatakeyama et al., 1987), and also from aqueous processing of volatile organic compounds (VOCs) and intermediates (Lim et al., 2005; Yu et al., 2005; Carlton et al., 2006; Sorooshian et al., 2006; Carlton et al., 2007; Sorooshian et al., 2007; Lim et al., 2013; Zhang et al., 2016). High loadings of diacids have been recently reported in aerosols significantly influenced by biomass burning emissions (Narukawa et al., 1999; Kundu et al., 2010; Kawamura et al., 2013).

Previous research has indicated that biomass combustion and fossil fuel combustion are the primary sources (Kawamura et al., 2013; Narukawa et al., 1999) while atmospheric diacids and related

compounds are primarily formed by the photochemical oxidation of precursors such as volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and fatty acids (Kawamura et al., 1996; Bikkina et al., 2014). Such secondary formation processes are related to the nature of the aerosol aqueous phase, such as aerosol liquid water content (ALWC) and acidity, as well as the abundance and composition of the precursors (Wang et al., 2016, 2018). Also, dicarboxylic acids (C2-C12) and their precursors, such as ketocarboxylic acids and -dicarbonyls, are abundant and ubiquitous in the atmosphere (Hoque et al., 2017; Wang et al., 2018). Because dicarboxylic acids and related compounds are highly water-soluble, they can act as cloud condensation nuclei (CCN) and thus may play an important role in cloud formation and climate change (Kawamura and Usukura, 1993; Sorathia et al., 2018; Zhang et al., 2016).

As major products of photosynthesized carbon in ecosystems, saccharides (monosaccharides, disaccharides) and their derivatives are also dominant in the atmosphere. They derived from primary thermal degradation of cellulose and hemicellulose present in biomass that have also been proposed as primary tracers for BB emissions (Alvi et al., 2020; Gonclaves et al., 2021). Thus, another aspect of this study is the estimation of sugars that are emitted or generated during biomass burning. Their contribution is important, considering that approximately 13–26% of the mass of total compounds identified in continental aerosols were saccharides, and this number can reach as high as 63% in oceanic aerosols (Li et al., 2021; Vincenti et al., 2021). Atmospheric saccharides derived from different source types are mainly composed of: (a) monosaccharides including D(+)-glucose (dextrose), D(−)-fructose (levulose), D(+)-xylose, etc. and disaccharides such as D(+)-sucrose and D(+)-trehalose (mycose), among others released by microorganisms, plants, animals and soil suspension, (b) sugar alcohols or polyhydric alcohols (saccharide derivatives) such as D(+)-arabitol, D-mannitol, D-sorbitol (glucitol) and xylitol produced by fungi, lichens, bacteria and yeasts, and (c) anhydrosugars such as the three stereoisomers levoglucosan, galactosan and mannosan derived from primary thermal degradation of cellulose and hemicellulose (structural polysaccharides) present in biomass.

Such studies are critical for understanding the transport mechanism of aerosols and the dynamics of air quality in a specific region. Further the characteristics of organic aerosols revealed in this study may

also be used as fingerprints to identify the source regions of air pollutants. Results of this study would also enable the civic authorities to adopt measures to mitigate and control air pollution in the city and impose restrictions on the use of biomass fuels for domestic and commercial consumption in the city as well as make the general public aware of not using these fuels for space heating purposes.

Literature Review

International Status

Several studies on biomass burning and its emissions have concluded that biomass burning including both open wildfires and constrained residential combustion is a large source of atmospheric particulate matter (PM) with significant impacts on global climate, regional air quality, and human health (Andreae, 1991; Levin et al., 2010; Wong et al., 2019; Zong et al., 2015). As per the study of Cheng et al., 2014 it had been observed that in Yangtze River Delta (China), the biomass burning contributed 37% of ambient $PM_{2.5}$ concentrations during the harvest period. Another study reported by Huang et al., 2014 and Wang et al., 2015 resulted that the impact of biomass burning on increased $PM_{2.5}$ concentrations.

In the context of sources of biomass burning, Li et al., 2007; Mellouki et al., 2015; Li et al., 2016; Sun et al., 2016 stated that the $PM_{2.5}$ is primarily composed of carbon, potassium, and chlorine, with emission factors of 7.64.1 g/kg and 11.71.0 g/kg for wheat straw and maize stover, respectively. It also stated that 12.1-24.2% of nitrogen is released as nitrogen-based trace gases and 11.0-24.9% of sulphur is released as SO_2 during biomass combustion. Another study by Zhang et al., 2011 investigated the emission of polycyclic aromatic hydrocarbons (PAHs) and particle size distribution by the combustion of agricultural residue and reported the PAHs emission factors of rice (5.26 mg kg^{-1}), (1.37 mg kg^{-1}) and corn straws (1.74 mg kg^{-1}). Also, the study by Zhang et al., 2010 reported that the BB also contributed to the generation of organic aerosols (OAs) that are mostly water soluble and have a substantial impact on climate change.

According to Graham et al., 2002; Decesari et al., 2006; Odabasi et al., 2009; Tsai et al., 2010; Smith et al., 2015, the measurement of molecular marker compounds in air samples is helpful to examine the major emission sources of atmospheric aerosols. It can also provide new insights into the atmospheric transport and source contributions to OAs. Hence, as per the studies done by Simoneit et al., 2004;

Cheng et al., 2014; Kalogridis et al., 2018 it has been observed that anhydrosugars and dicarboxylic acids can be used as the molecular markers of biomass burning. Similarly, Oros et al., 2001; Cao et al., 2017; Bhattarai et al., 2019 found a strong link between diacids and sugars and biomass burning. According to their findings, the BB fills the ambient air with high $PM_{2.5}$ concentrations, dicarboxylic acids, and levoglucosan (sugar) throughout the harvest season mainly during autumn, and chosen ratios of these chemicals can be utilised as tracers for the secondary generation of organic aerosols. During the harvest season, the concentration of various dicarboxylic acids and associated compounds rose by >20 times with various factors for various organic compounds. Monosaccharide derivatives from cellulose breakdown, along with tiny quantities of straight chain, aliphatic, oxygenated compounds, and terpenoids from plant waxes, resins/gums, and other biopolymers, make up the majority of organic components from biomass fire emissions, according to a study by Li et al., 2021, with similar results as Chen et al., 2017 and Wan et al., 2019. The major indicators for biomass burning include levoglucosan from cellulose, various mono and di carboxylic acids, and several other significant organic chemicals such as vanillic acid, vanillin, syringic acid, 4-hydroxybenzoic acid, syringaldehyde, dehydroabietic acid, and p-coumaric acid.

According to Khwaja et al., 1995 and Kawamura et al., 2015, the molecular distribution of diacids in marine aerosols is due to primarily continental outflows during the spring and winter seasons, and the abundance of different diacids varies by physiological area, with oxalic acid (C_2) being more abundant in marine aerosols than malonic acid (C_3) and succinic acid (C_4) being more prominent in polar regions. Zhao et al., 2018 elucidated the seasonal variation, molecular distribution, and stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids, and -dicarbonyls. They observed that the concentrations of dicarboxylic acids, oxoacids, and dicarbonyls ranged from 110 to 2580 ng m^{-3}, 9.50 to 353 ng m^{-3}, and 1.50-85 ng m^{-3} respectively. The ambient concentrations of phthalic acid (37.9±27.3ng m^{-3}) and terephthalic acid (48.7±51.1 ng m^{-3}) were also discovered in this study, a plastic waste burning tracer with higher concentrations in the winter owing to fossil fuel combustion and plastic waste incineration. Another studies by Kawamura et al., 1993; Ikemori et al., 2018; Sato et al., 2021 investigated the precursors of dicarboxylic acids and found that the C_4 diacids like maleic acid, succinic acid, fumaric acid, malic acid, meso-tartaric acid can be produced by the photo-oxidation of

toluene while photo-oxidation of naphthalene can generate maleic acid and fumaric acid. Another fruitful study by Marzelloni et al., 2007 and Bhattarai et al., 2019 investigated another tracer of BB which are sugars and found the emission of levoglucosan, methoxy phenols and organic acids from different burning sources. Similarly, Scaramboni et al 2014 observed that total sugar can also be an alternative tracer of biomass burning, instead of levoglucosan, as this study found that the concentration of total sugar in the aerosol ranged from 0.28 to 12.5μg m^{-3} and the emission found higher at night and a significant correlation between levoglucosan and total sugar. Medeiros et al., 2007 and Fu et al., 2012 and recent study by Liang et al., 2021 investigated sources and seasonal variation of water-soluble sugars in aerosols present in the form of primary sugars and sugar alcohols. Thus, by using the gas chromatography-mass spectroscopy this study estimated the seasonal variation in concentration of sugars within the range of 6.8-1760 ng m^{-3} and also concluded that the total identified sugars have the highest concentration in April (harvest season).

Thus, diacids and sugars have been proved good biomass markers to trace the sources of biomass burning hence, study by Caseiro et al., 2007 showed an improved method for the quantification of primary sugar, sugar alcohol and anhydrosugars in atmospheric aerosols mainly generated by the biomass burning. This study used high-performance anion exchange chromatography (HPAEC) with pulse amperometric detection (PAD) and observed 50 ng m^{-3} of levoglucosan in air and elevated concentration of 700 ng m^{-3} during winter due to biomass burning. Also, the recent study of Li et al., 2020 characterized sugars in aerosol particles by using high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS). As a result, this study successfully quantified monosaccharide sugar (inositol), disaccharides (sucrose, trehalose), sugar alcohols (arabitol, threitol, and sorbitol) and anhydrosugars (levoglucosan) with the concentration levels of 10 μg L^{-1}, 100 μg L^{-1} and 500 μg L^{-1} in five replicates.

National Status

Study of Abdurrahman et al., 2020 on stubble burning suggested that it contributes to the increased concentration of carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x) and methane (CH_4) and the most controversial pollutants of the recent studies particulate matters (PM_{10} and $PM_{2.5}$). This study estimated the generation of 352 Mt of stubble each year in India and the

major cause behind this is the wheat (22%) and rice (34%) stubble. Another marked study by Ravindra et al., 2018 with similar results estimated the emission of 824 Gg of $PM_{2.5}$, 812 Gg of PM_{10}, 58 Gg of elemental carbon (EC) and 239 Gg of organic carbon (OC) during crop residue burning. Highlighting other consequences of biomass burning, study by Ningombam et al., 2019 estimated the increased heating rates in the atmosphere by 3.79% and 3.44% during fire and non-fire events respectively over the Lahore. Thus it stated that the biomass burning contribute to the increased surface radiative and atmospheric forcing. Similar results have also been observed by Singh et al., 2018 and Ghosh et al., 2019 over Indo-Gangetic Plains (IGP) and Kolkata respectively. In the context of biomass burning, a significant seasonal variation of particulate matter has been observed for instance, Ojha et al., 2020 found the enhanced concentration of $PM_{2.5}$ (>100 μgm^{-3}) during post-monsoon over the IGP region and a widespread enhancement in concentration during winter. Study by Singh et al., 2017, Organic aerosol (OA) constitutes the major portion of particulates over IGP region mainly during post-monsoon and winter which link it with biomass burning, coal combustion and vehicular emissions.

Biomass burning and combustion of biofuels are identified as the major sources of OAs in eastern central India (Giri et al., 2013; Nirmalkar et al., 2015; Deshmukh et al., 2016). Verma et al. (2007, 2008, 2010) found high loadings of fine mode aerosols (average 239 $\mu g\ m^{-3}$) and coarse mode aerosols (average 245 µg m–3) as well as gaseous pollutants such as sulfur dioxide (SO_2) (average 95.2 $\mu g\ m^{-3}$) and nitrogen dioxide (NO_2) (average 115 $\mu g\ m^{-3}$) in the atmosphere of eastern central India. The results of Giri et al. (2013) revealed that the dominant components of OAs in eastern central India are from fossil fuel utilization and the burning of biomass and plastics. Nirmalkar et al. (2015) also reported biomass burning and fossil fuel combustion as the dominant emission sources leading to high levels of OAs in eastern central India. Rastogi et al., 2016 studied the temporal variability of primary and secondary organic aerosols and impact of biomass burning aerosols at Patiala. They observed that emissions from biomass burning aerosols dominated the abundances of carbonaceous aerosols in the area. Ghosh et al., 2019 studied the impact of biomass burning plumes on the size-segregated aerosol chemistry over Kolkata. Most recently Lalchandani et al., studied the effect of biomass burning on $PM_{2.5}$ composition and secondary aerosol formation during post-monsoon and winter haze episodes in Delhi. They found that BB aerosol was dominant in all haze periods with the majority of its present in

highly aged form. The study also concluded that open biomass burning emissions undergo rapid nighttime oxidation resulting in high yields of secondary organics and inorganics (Lalchandani et al., 2022).

Objectives

In-situ measurements to examine the impact of biomass burning on atmospheric composition are favoured over IGP because India is an agricultural country. The crop residue burning often takes place in the months from October to November and from April to May. As a result of the substantial crop residue burning high loadings of fine mode aerosols and coarse mode aerosols as well as gaseous pollutants have been observed in the atmosphere. Additionally, winter haze events are significantly impacted by biomass burning emissions, most likely from local roadside trash, coal, cow dung and wood burning for cooking or heating. Despite the environmental relevance of biomass burning emissions, no study has been conducted on the characterization of biomass burning aerosols in the atmosphere of Agra. Thus, this study is focussed on the estimation of biomass tracers (Diacids and Sugars) along with the concentration of trace gases, elemental and organic carbon (OC/EC) in particulate matter to better understand biomass burning and their sources and methods to infer burning types.

Therefore, to supplement the scarcity of observations in the atmosphere of Agra the study has been planned to:

- Determine the chemical composition of $PM_{2.5}$ and PM_{10} aerosols (water soluble ions WSI, water soluble organic compounds WSOC, diacids and sugars, elemental and organic carbon, polyaromatic hydrocarbons) during biomass burning and non-biomass burning periods.
- Assess the influence of biomass burning on aerosol composition through the biomass tracers (diacids and sugars), meteorological factors and air mass trajectories.
- Study the impact of biomass burning on levels of trace gases namely ozone, carbon monoxide and oxides of nitrogen.
- Assess the mutagenic and oxidative potential of aerosols and perform health risk assessment of exposed population during the biomass burning and non-biomass burning periods.

Proposed Methodology

SAMPLING SITE

Sampling will be carried out at two sites in Agra that are, the roof of Science Faculty Building, Dayalbagh Educational Institute (University Campus) and at a residential cum traffic area near Rambagh. Dayalbagh is a semi-urban site surrounded by a small residential community and agricultural fields and the industrial sector of Agra is about 10 km away. Other site Rambagh is a residential cum traffic site with high mobility and the NH-2 highway is nearly 100 m away from the sampling site.

Agra lies in a semi - arid zone, adjacent to the Thar Desert of Rajasthan. Agra has continental type of climate. The city observes dry climate during summer and winter. Annual rainfall is about 760.7 mm with 90% being receivedduring the monsoon season (July–August).

SAMPLING AND ANALYSIS:

Sampling: Collection of aerosol samples (for $PM_{2.5}$ and PM_{10}) will be carried out using a High volume sampler, Envirotech APM 550 on pre-combusted (pre-heated at 900 °C for 3 hours) 47 mm quartz microfiber filters (Pallflex, Tissuquartz). The exposed filters will be stored in a refrigerator at ~4 °C until chemically analyzed. The PM mass concentrations will be determined gravimetrically using electronic microbalance (Mettler AJ150). Each filter will be weighed before and after sampling, and the net mass will be obtained by difference of two weights.

EXTRACTION AND ANALYSIS:

Water soluble inorganic ions: For analysis of ions (Cl^-, NO_3^-, SO_4^{2-}, F^-, Na^+, K^+, NH_4^+, Ca^{2+}), one-third of sampled filter paper will be cut and extracted ultrasonically for 30 min in 15 mL deionized water. After ultrasonication, the extracts will be filtered through microporous membrane filter paper (Sartorius 393). The anions and cations will be analyzed by ion chromatography (IC), Dionex ICS 1100 (isocratic system). Anions will be analyzed by an analytical column (AS11), ASRS Ultra anion self-regenerating suppressor, and a guard column (AG11) using an eluent of 6.0 mM NaOH at a flow rate of 1.0 mL min^{-1}. Cations will be analyzed using a guard column (CG12A), analytical column (CS12A), cation self-regenerating suppressor (CSRS) and 20.0 mM MSA (Methane Sulphonic Acid) as eluent at a flow rate of 1.0 mL min^{-1}.

Trace Metals: One-fourth fraction of exposed filter paper will be digested in a Microwave digester with 6 to 8ml of reagent grade HNO_3 (65%, Merck Supra pure). After filtering the digested sample through a microporous membrane filter (Sartorious 393) the solution will be made up to 50 ml with distilled water in PTFE bottles. The samples, thus, prepared will be subjected to analysis of metals (Cr, Cd, Mn, Zn, As, Co, Pb, Cu and Ni) by ICP-OES (Agilent Technologies).

Organic compounds: Other half portion of exposed filter paper will be used to analyze organic compounds (dicarboxylic acids, sugars, PAHs).

Diacids: The filter samples will be extracted for low molecular weight di-carboxylic acids with pure water prepared by distillation after $KMnO_4$ oxidation of Mili Q water. The water extracts will be concentrated using a rotary evaporator under vacuum. The diacids and related compounds will be reacted with a 14% BF_3/n-butanol at 100 °C for 60 min to derivatize. After the reaction, the derivatives will be extracted with n-hexane, washed with pure water, and dissolved in 50 µL of n-hexane. Samples will be analysed via Gas chromatograph equipped with a split/ splitless injector, and a FID (flame ionization detector) coupled with MS (GC-MS).

Sugars: A portion of filter paper will be extracted for 30 min with 20 mL of dichloromethane/methanol (4:1, v/v), using an ultrasonic bath. The extraction procedure will be repeated twice, and the combined solution will be evaporated to approximately 1.5 mL. This solution will be filtered (0.45 mm) and completely dried under nitrogen flow prior to derivatization for 1 h at 70 °C, using 40 mL of N,O-bis-(trimethylsilyl)- trifluoroacetamide (BSTFA), with 1% trimethylchlorosilane (TMCS) and 10 µL of pyridine. The resulting compound will be dried in an ice bath, and resuspended in 25 µL of hexane. An aliquot of 1.0 µL will be injected into a Gas chromatograph coupled to a mass spectrometer (GC-MS) for analysis.

Polyaromatic hydrocarbons (PAHs): PM-bound PAHs will be extracted by ultrasonic agitation with dichloromethane for 1 hour with intervals of 10 min after every 15 min to ensure maximum recovery. The extract will be purified by means of clean up in silica gel column to remove elements interfering in the analysis. The extract will be passed through a glass column and eluted with dichloromethane to obtain fraction enriched with PAH. PAH - fraction will then be concentrated to 1.5 mL by a rotary evaporator and stored in Teflon vials at low temperature till analysis. 16 parent PAHs and their oxy

and nitro-derivatives will be analysed in selected ion monitoring mode according to their m/z ratio by using a Gas-Chromatograph-Mass Spectrometer (GC-MS).

Trace Gas Measurement: Concentrations of Trace gases Ozone, NOx and CO will be recorded by Online Analyzers (Thermo Fisher and Teledyne).

Recording of Meteorological Parameters: Meteorological parameters (Temperature, Solar radiation, Wind Direction and Wind speed, Precipitation, Relative humidity and Pressure) will be recorded by automatic weather station.

CALCULATIONS AND DATA INTERPRETATION:

- *Levels and Trends in the Chemical Composition of Particulate Matter:*

Various statistical techniques like significance tests, correlation and multiple regression analyses of Variance would be used to reveal atmospheric processes and atmospheric chemistry, trends and seasonal variations of different chemical constituents of particulate matter as well as study the influence of meteorological parameters in controlling the atmospheric levels and processes.

- *Identification of Molecular distribution, Relative Abundances of Primary Organic Aerosols (POA) and Secondary Organic Aerosol (SOA) and Biomass Burning Type:*

The specific Tracer ratio method is the most common and basic method for identifying the type of biomass burning in the atmosphere. These include the ratios of levoglucosan to mannosan, levoglucosan to OC, levoglucosan to potassium and ratios of different diacids (vanillic to syringic acid, syringic to 1-hydroxybenzoic acid etc), K^+/EC, OC/EC, K^+/OC, EC/OC, Ratios among different PAHs, WSOC/OC etc.

Few Samples would also be analysed through Field Emission Scanning Electron Microscope (FE-SEM) to study the morphological characteristics of the particulate matter during specific events like haze and non-haze period, diwali and holi period, dust storm events etc. This analysis would further corroborate the findings.

- *Source Identification and Apportionment:*

Source identification and apportionment will be attempted by data reduction techniques like principal component analysis, Positive matrix factorization, Source tracer ratio method as well as Backward Air Trajectory Methods will be used to ascertain the local and regional sources of

pollution. Statistical software like SPSS, Trajstat, Origin will be used for these computations.

- *Health Risk Assessments:*

  Health Risk assessment to the local inhabitants would be conducted using standard EPA Health Risk Assessment Models estimating the Hazard Index and Hazard Quotient as well as Incremental Lifetime Cancer Risk due to exposure to the ambient levels of metals, and Polyaromatic hydrocarbons. Simultaneously the mutagenic potential of the fine particulate matter would be estimated in few representative samples in each season by the Ames assay while the oxidative potential of these aerosols would also be estimated through the a cellular methods of Dithiothrietol (DTT) and Dichlorofluorescin method (DCFH).

- *Ames Assay*

  Ames test will be performed to test mutagenicity (i.e., frameshift and base-pair mutation with S. typhimurium TA98 and TA100 strains, respectively) for each combustion experiment. Particulate phase PAH extracts will be dissolved in 4 mL of dimethyl sulfoxide (DMSO) immediately before the Ames tests will performed. The bacterial strains will initially be cultured in tubes containing beef extract agar medium for 15− 18 h before the experiment. The test will be performed in plates containing two distinct layers of agar, that is, a bottom layer of 25 mL of agar solution (glucose minimal agar) to provide support media and 2 mL of top agar for applying the test chemical and the desired strain. The bottom agar will be made of Vogel−Bonner minimal media E (50×), agar, and glucose. The top layer of agar solution will be composed of agar, NaCl, histidine, and biotin. After solidification of agar solution in the plates, organic extract will be applied to each plate in fixed doses. Plates will be incubated in an inverted position for 63 h at 37 °C in the dark. Revertant colonies formed after incubation in each plate will be counted using a hand-held digital colony counter.

Expected Outcomes

The main outcomes of this study will be to gain an insight into chemical composition of particulate matter and source identification. Secondly the results of this study would also reveal how dust and aerosols transported from IGP and the crop residue burning and major biomass burning areas, alter the distribution and composition of PM and how transported aerosols from these regions recombines with

anthropogenically emitted local PM. This study will also be focusing on the fundamental understanding of the factors affecting PM toxicity, which are mainly chemical composition, size and solubility. These measurements are also important for the assessment of regional air quality and transformation processes during the long-range transport of important gaseous and particulate species; and in designing and planning appropriate mitigation strategies to reduce emission from sources. The results of this study would increase awareness and educate the farmer community to promote alternative uses of crop residues in particular like mushroom cultivation, production of biochar and biofertilizers, use in the packaging industry, use as mulching material etc. Investments to stop crop burning and offer farmers alternative crop residue disposal solutions are likely to improve population-level respiratory health and yield major economic returns. The results of this study will further fill knowledge gaps and inform evidence-based interventions that protect human health.

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